

## III.A.12 Continuous Process for Low-Cost, High-Quality YSZ Powder

### Objectives

- Develop a robust process for producing yttrium-stabilized zirconia (YSZ) powder that can be tailored to meet the SECA industry team needs.
- Produce YSZ powder in 5-10 kg batches, and demonstrate reproducibility of the process.
- Demonstrate the advantages of tailoring YSZ powder characteristics to specific requirements of fabrication processes used in SOFC manufacture.
- Demonstrate the process provides YSZ powder at low manufacturing cost.
- Demonstrated sintered YSZ ceramics with high ionic conductivity ( $>0.04$  S/cm at  $800^{\circ}\text{C}$ ), equivalent to the best values reported in the literature.
- Demonstrated a high surface area and fine particle size grade of YSZ powder that can be sintered at low temperatures ( $1,200^{\circ}\text{C}$  to  $1,250^{\circ}\text{C}$ ).
- Provided samples of low-temperature sintering grade YSZ electrolyte powder to one of SECA's industry team leaders.
- Demonstrated that the manufactured cost of YSZ powder produced using the process will be less than \$27 per kilogram at large production volumes.

### Approach

- Use of chemical precipitation methods to produce hydroxide precursors that can be converted into crystalline YSZ via thermal treatments.
- Use of ball milling and attrition milling methods to reduce particle size of YSZ powders to below one micron.
- Use of uniaxial and isostatic pressing methods followed by sintering to fabricate ceramic samples for density and ionic conductivity measurements.

### Accomplishments

- Established a homogeneous precipitation process for preparing an yttrium-zirconium hydroxide precursor, which can be converted to crystalline YSZ via calcination.
- Established calcination and milling methods to prepare YSZ powders with controlled surface area and particle size distribution.
- Demonstrated that YSZ powder produced by the process can be sintered to densities greater than 98 percent theoretical at temperatures less than  $1,400^{\circ}\text{C}$ .

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### Introduction

One of the current barriers to reducing the manufacturing cost of SOFCs is the high cost of some of the critical raw materials. The availability of a low-cost, highly reliable and reproducible supply of engineered raw materials is needed to assure successful commercialization of SOFC technology. The yttrium-stabilized zirconia (YSZ) electrolyte material is a primary ingredient for two of the three layers comprising an SOFC element: the dense electrolyte layer and the porous nickel-based cermet (Ni/YSZ) anode layer. In addition, YSZ often is used as a performance-enhancing additive to lanthanum strontium manganite (LSM) based cathode layers. In practice, the same YSZ raw material is used for each of the component layers, even though different fabrication processes are used for each layer. Significant opportunities for performance optimization and cost reduction would be possible if the YSZ raw material is tailored for each component layer. This project focuses on the development of YSZ powder synthesis technology that is "tailored" to the process-specific needs of different SOFC designs being developed under DOE's Solid-State Energy Conversion Alliance (SECA) program.

### Approach

NexTech's approach to developing a low-cost YSZ electrolyte powder production process is based on the following principles: (1) the process must be scaleable to low-cost, high-volume production; (2) the process must be sufficiently versatile so that powder characteristics can be tailored to a specific customer's requirements; (3) the process must be reliable, providing consistent batch-to-batch quality; and (4) the process must provide a relatively pure YSZ powder that meets performance criteria relative to particle size, surface

area, sintering activity, and ionic conductivity. With the homogeneous precipitation process that was developed in this project (see Figure 1), the pH and solids content remain constant throughout the process, which is the key to achieving uniformity and reproducibility of the finished product. Another attribute of the homogeneous precipitation process is that it can be made continuous with constant replenishment of the feed solutions. This provides considerable cost and reliability advantages, relative to current chemical synthesis processes.

In the project, synthesis studies are being conducted to identify optimum precipitation conditions for producing hydrous oxide precursors. These precursors then are processed into YSZ powders by washing and drying of the precipitates, calcination of the dried precursor to form a crystalline YSZ powder with targeted surface area ( $\sim 10 \text{ m}^2/\text{gram}$ ), and milling of the calcined YSZ powder to sub-micron particle size. The YSZ powders are subjected to a comprehensive characterization protocol, involving x-ray diffraction, chemical analyses, particle size distribution, surface area measurements, and sintering studies. Performance of sintered YSZ ceramics are being assessed by density measurements, ionic conductivity measurements, mechanical property measurements, and scanning electron microscopy.

## Results

In this project, NexTech has demonstrated a laboratory-scale continuous (homogeneous) precipitation process for YSZ electrolyte powder with equivalent, and in some ways superior performance to YSZ powder that is commercially available from non-domestic suppliers. Key results of the project are discussed below:

- The initial precipitation conditions were shown to have a profound effect on the performance of fully processed (calcined and milled) YSZ powders. After optimization of precipitation conditions, YSZ powders produced by NexTech's baseline process

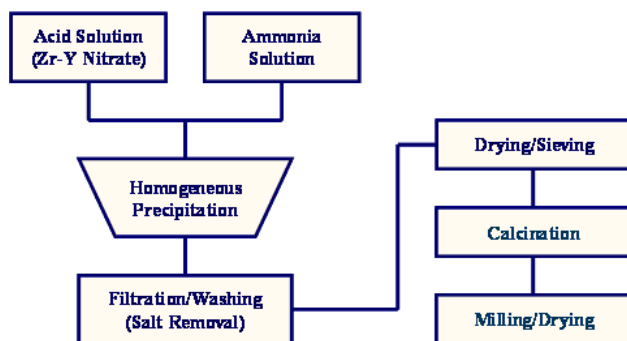


FIGURE 1. Homogenous Precipitation Process for YSZ Powder

sinter to high densities ( $>98$  percent theoretical) at temperatures of  $1,300^\circ\text{C}$  and higher. The NexTech powder also exhibits improved low-temperature sinterability, compared to commercial powder (Tosoh, TZ-8Y) with similar surface area (see Figure 2).

- NexTech demonstrated reproducibility of its synthesis process by producing three separate batches of YSZ powder, and characterizing these powders through all stages of processing. Particle size distribution measurements (see Figure 3) indicated average particle sizes of 0.30, 0.27 and 0.31 microns, and surface areas of the three powders ranged from  $13.9$  to  $14.5 \text{ m}^2/\text{gram}$ . Sintering performance (see Figure 4) and ionic conductivity (see Figure 5) were identical for the three batches (within experimental error of the measurements).
- NexTech demonstrated improved densification through doping with alumina ( $\text{Al}_2\text{O}_3$ ), nickel oxide ( $\text{NiO}$ ), manganese oxide ( $\text{Mn}_2\text{O}_3$ ) and cobalt oxide ( $\text{CoO}$ ) dopants, especially at low sintering temperatures (less than  $1,300^\circ\text{C}$ ).  $\text{NiO}$  and  $\text{Mn}_2\text{O}_3$  dopants resulted in significant depression of ionic conductivity, whereas this effect was less pronounced with  $\text{Al}_2\text{O}_3$  and  $\text{CoO}$  dopants (depending on the dopant amount and method of incorporation). Results obtained with  $\text{CoO}$  dopants are presented in Figures 6 and 7. With a 0.1 wt% addition of  $\text{CoO}$ , the sintering temperature was reduced by about  $50^\circ\text{C}$ , with little change in ionic conductivity at  $800^\circ\text{C}$ . With increased cobalt doping (1 wt%), the sintering performance is further improved, but with a significant loss of ionic conductivity.
- NexTech's synthesis process also was demonstrated for scandium-stabilized zirconia ( $\text{ScSZ}$ ) electrolyte compositions, both partially stabilized  $\text{ScSZ-6}$  and fully-stabilized  $\text{ScSZ-10}$  compositions. The

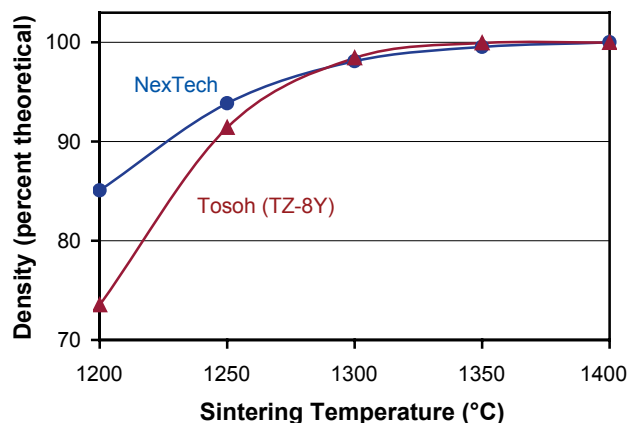
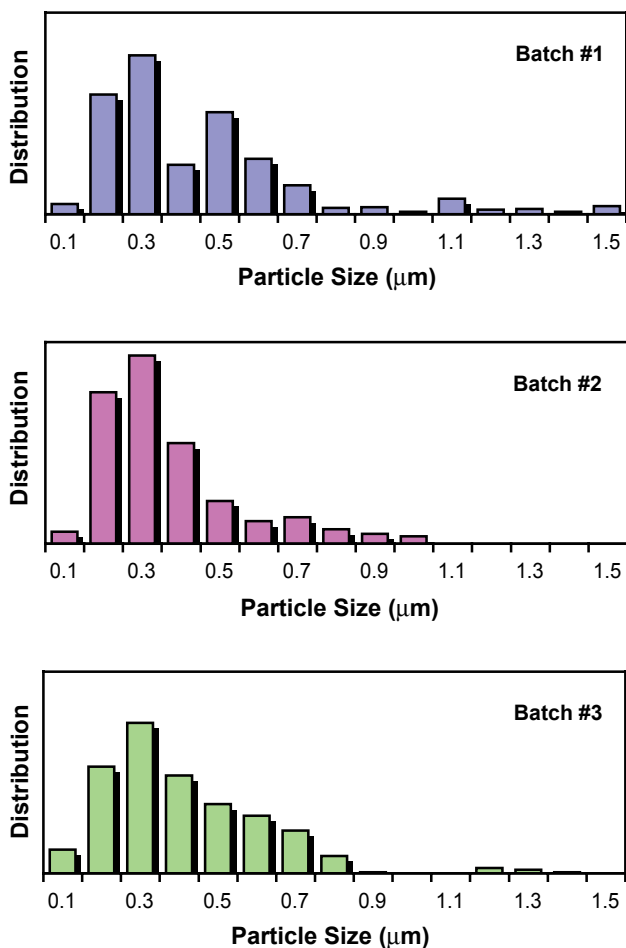
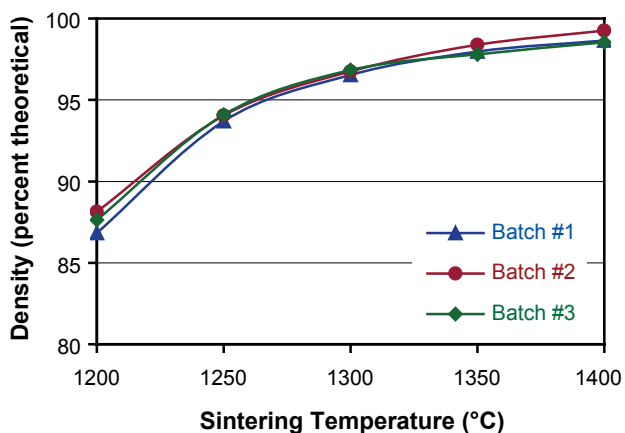


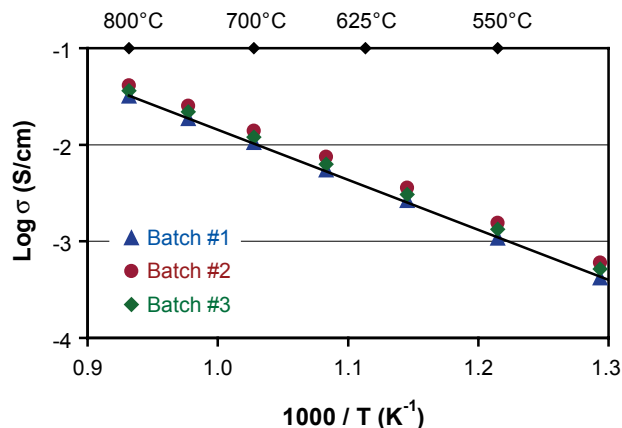
FIGURE 2. Sintering Performance of NexTech's YSZ Powder (baseline process), Compared to Commercially Available YSZ Powder (Tosoh, TZ-8Y)



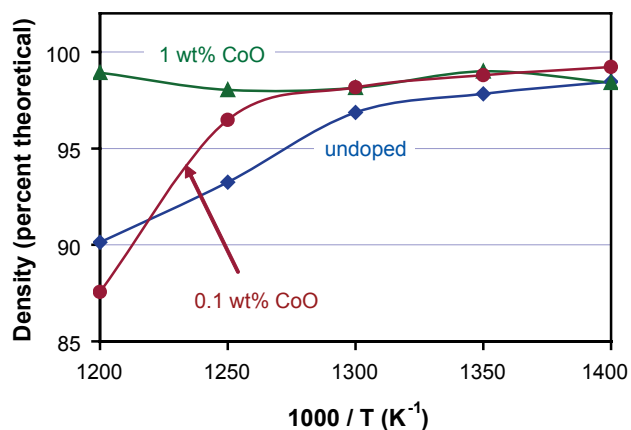
**FIGURE 3.** Particle Size Distributions of YSZ Powder from Three Separate Batches



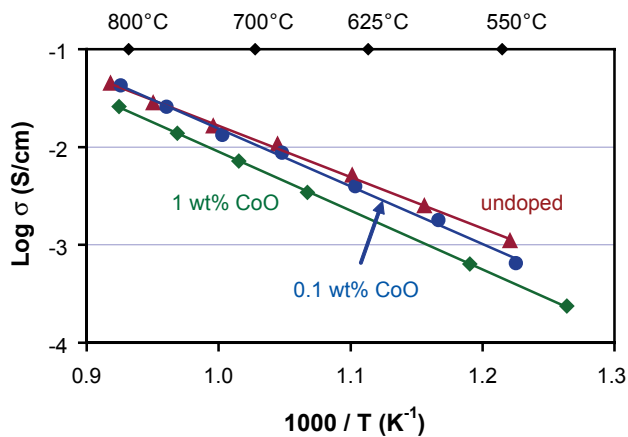
**FIGURE 4.** Sintering Performance Data for YSZ Powders from Three Separate Batches



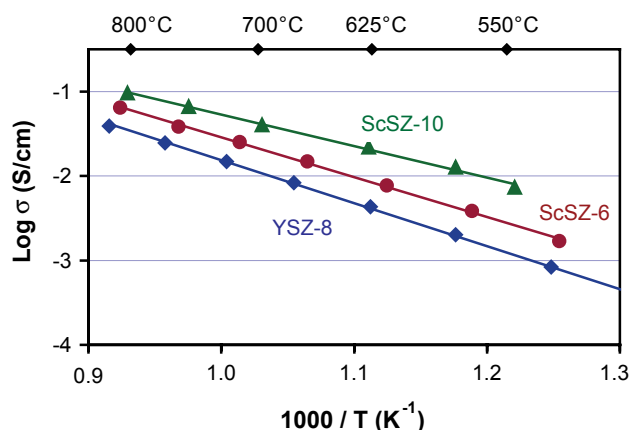
**FIGURE 5.** Ionic Conductivity Data for YSZ Ceramics Prepared from Three Separate Batches



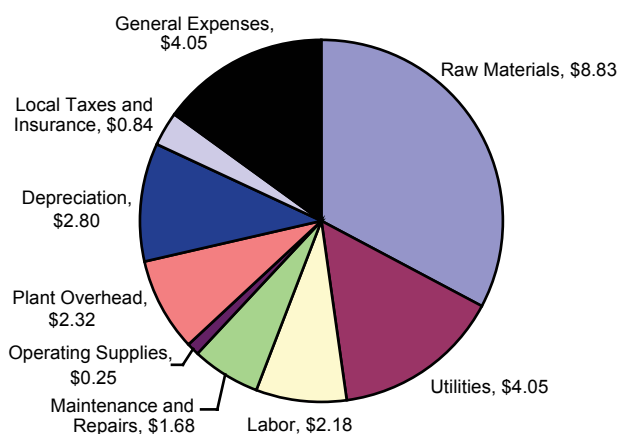
**FIGURE 6.** Effect of Cobalt Doping on Sintering Performance of YSZ Powder



**FIGURE 7.** Effect of Cobalt Doping on Ionic Conductivity of Sintered YSZ Ceramics



**FIGURE 8.** Ionic Conductivity of Yttrium Stabilized and Scandium Stabilized Zirconia Ceramics



**FIGURE 9.** Results of Manufacturing Cost Analysis

increased conductivity of ScSZ electrolytes was confirmed (see Figure 8).

- A manufacturing cost analysis confirmed that YSZ powder prepared by NexTech's homogeneous precipitation process could be manufactured for a cost of \$27 per kilogram (see Figure 9). This analysis was based on a production volume of 500 metric tons per year, which is a fraction of the volume necessary when SOFC are in full-scale production.

## Conclusions

In this project, NexTech Materials developed a low-cost and flexible homogeneous precipitation process for production of high quality YSZ electrolyte powders required for the manufacture of solid oxide fuel cells. Work on the project involved development, refinement and scale-up of the powder synthesis

process, along with comprehensive characterization by particle size distribution measurements, surface area analyses, sintering performance evaluations, and ionic conductivity measurements. The two primary advantages of the YSZ powder produced by the process, compared to commercially available YSZ electrolyte powders, included tailorability of particle size and surface area and low temperature sintering capability. Specific conclusions from the work on this project are provided below:

- The homogeneous precipitation process developed on this project provides a hydrous oxide precursor that can be processed into high quality YSZ electrolyte powder. The process involved simultaneous pumping of an acidic solution containing yttrium and zirconium salts and a basic solution containing ammonium hydroxide to form a slurry of yttrium-zirconium hydroxides (or hydrous oxides). The precipitation process is controlled so that the pH and solids content of the hydrous oxidize precursor is maintained at a constant level throughout the precipitation process. Specific variables of the precipitation process that are important to achieving high performance of the resulting YSZ powder include precipitation pH, dilution levels of the starting acid and base solutions, and the pump flow rates of the starting acidic and basic solutions.
- Processing of the hydrous oxide precursor into YSZ electrolyte powder involves the steps of washing of the precipitated slurry (to remove residual salts), modification of the slurry, either by addition of surfactants or solvent exchange with isopropyl alcohol, to minimize unwanted agglomeration during drying, drying of the hydrous oxide precursor into an amorphous powder, calcination of the precipitate to form a crystalline YSZ powder, and milling of the YSZ powder to a targeted surface area (10-15 m<sup>2</sup>/gram) and particle size (<0.5 μm). It was found that all of these processing steps had an impact on the sintering performance of the YSZ powder.
- The milling step in the process was found to be critically important for producing high performance YSZ electrolyte powder. In particular, high energy milling processes were required to achieve optimized particle size distributions and enhanced sintering performance. The elimination of particles greater than one micron in size led to significant improvements in sintering performance, especially at temperatures of less than 1,300°C. The use of milling aids was found to help the milling process, and two especially suitable milling additives were identified.
- Calcination and milling methods were established for controlling surface area and particle size of YSZ powders within the targeted surface area

and particle size ranges (10-15 m<sup>2</sup>/gram and 0.3 to 0.4 microns, respectively). The synthesis and processing methods were further refined to produce YSZ powders with improved low-temperature sinterability and equivalent ionic conductivity compared to commercially available YSZ powder. The process provides a YSZ powder that can be sintered to high density (>95 percent theoretical) at temperatures as low as 1,250°C.

- A number of oxide additives were evaluated and found to improve sintering performance of YSZ electrolyte powders produced by the process. Nickel, manganese, and aluminum oxide dopants (at levels of 0.1 to 1.0 wt%) all were found to be effective for increasing sintered densities and reducing sintering temperatures. However, these dopants led to significant reductions in ionic conductivity, even at low dopant levels. Cobalt oxide dopants, on the other hand, were found to improve sintering performance without negative impacts on ionic conductivity when added in sufficiently low levels (~0.1 wt%).

- All of the unit operations associated with the synthesis and processing of YSZ powders by the homogeneous precipitation process were scaled up at NexTech to allow YSZ powder production at 10-20 kilogram batch sizes. A number of processing studies were performed to characterize each step of the process to aid identification and specification of manufacturing scale equipment for full-scale production. A manufacturing cost analysis was performed, which confirmed that YSZ powder produced by the continuous precipitation process would have an estimated production cost of about \$27/kg for a 500-ton per year production rate. Opportunities for further cost reduction were identified.

### FY 2006 Publications/Presentations

1. S.L. Swartz, et al., *Continuous Process for Low-Cost, High-Quality YSZ Powder*, DOE Contract Number: DE-FC26-02NT41575, Final Report (March 31, 2006).